

→ From what's

Chemical kinetics:-

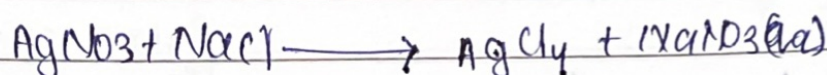
→ Chemical kinetics is the branch of physical chemistry which deals with the study of rate of reactions, the mechanism by which the reactions proceed and factors affecting rate of reaction.

→ On the basis of rate, chemical reactions are broadly divided into three categories:-

(a) Very Fast or instantaneous reactions:-

- Involve ionic species and known as ionic reactions.
- Take about 10^{-14} or 10^{-16} sec for completion.
- almost impossible to determine the rate of these reactions.

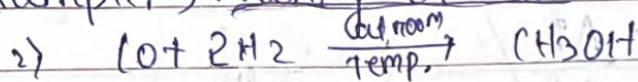
Example:-



(b) Very slow reactions:-

- These reactions proceed very slowly, may take days or months to show any measurable change at room temp.

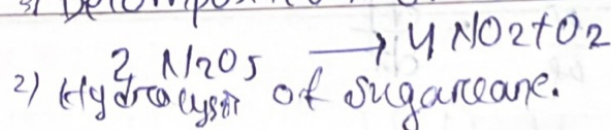
Example:- rusting of iron.



(c) Moderate or slow reaction:-

- These type of reactions proceed with a measurable rate at normal temp. and we can measure the rate of these reactions easily. Mostly these reactions are molecular in nature.

Example:- decomposition of N_2O_5



2) Hydrolysis of sucrose.

78

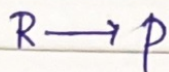
88

Rate of a Chemical Reaction:-

- Rate of reaction is defined as the change in concentration or pressure of Reactant or product per unit time.
- It is always a positive quantity.

$$\text{R.O.C} = \frac{\text{change in conc. of reactants / products}}{\text{time taken}}$$

consider a reaction;

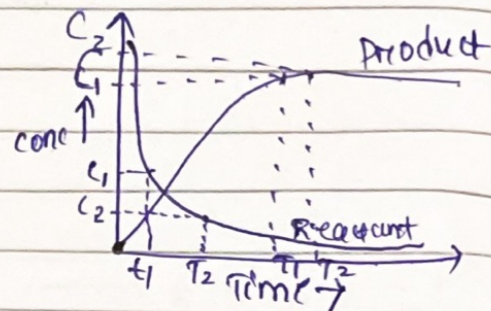


For reactant;

$$\text{rate} = -\frac{(C_2 - C_1)}{t_2 - t_1} = -\frac{\Delta[R]}{\Delta t}$$

For product;

$$\text{Rate} = \frac{C_2 - C_1}{T_2 - T_1} = +\frac{\Delta[P]}{\Delta T}$$



$[C] = \text{conc}$

Types of Rate of Reaction:-

A) Average rate of Reaction:-

→ The rate of reaction over a certain measurable period of time during the course of reaction is called average rate of Reaction.

→ It is denoted by $\bar{r}$ or r_{av} .

For Reaction, $A \rightarrow B$

$$\text{av/rate} = -\frac{(A_2 - A_1)}{t_2 - t_1} = -\frac{\Delta[A]}{\Delta t}$$

$[C] = \text{molar concentration}$

$$\text{av/rate} = \frac{B_2 - B_1}{T_2 - T_1} = +\frac{\Delta[B]}{\Delta T}$$

(B) Instantaneous R.O.R:-

→ The rate of Reaction at any particular instant during the course of reaction is called instantaneous Rate of Reaction.

For a reaction, $A \rightarrow B$

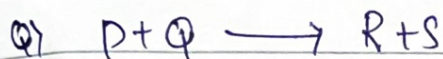
$$\text{Instantaneous rate} = \lim_{\Delta t \rightarrow 0} \text{Average rate}$$

For reactants,

$$r_{\text{inst.}} = \lim_{\Delta t \rightarrow 0} \left(-\frac{\Delta[A]}{\Delta t} \right) = -\frac{d[A]}{dt}$$

For products,

$$r_{\text{inst.}} = \lim_{\Delta t \rightarrow 0} \frac{\Delta[B]}{\Delta t} = \frac{d[B]}{dt}$$



For reactants,

$$r_{\text{inst.}} = \cancel{\lim_{\Delta t \rightarrow 0}} -\frac{d[P]}{dt} = -\frac{d[Q]}{dt} = +\frac{d[R]}{dt} = +\frac{d[S]}{dt}$$

Representation of Rate of Reaction and unit:-

Let us consider a reaction:- $m_1 A + m_2 B \rightarrow n_1 P + n_2 Q$

$$\text{Rate of disappearance of A} = -\frac{d[A]}{dt}$$

$$\text{Rate of " " B} = -\frac{d[B]}{dt}$$

$$\text{Rate of appearance of P} = +\frac{d[P]}{dt}$$

$$\text{Rate of " " Q} = +\frac{d[Q]}{dt}$$

$$\left. \begin{array}{l} r_{\text{inst.}} \\ -\frac{d[A]}{dt} \\ -\frac{d[B]}{dt} \\ +\frac{d[P]}{dt} \\ +\frac{d[Q]}{dt} \end{array} \right\}$$

$$\text{Rate of Reaction} = -\frac{1}{m_1} \frac{d[A]}{dt} = -\frac{1}{m_2} \frac{d[B]}{dt} = \frac{1}{n_1} \frac{d[P]}{dt} = \frac{1}{n_2} \frac{d[Q]}{dt}$$

Unit of R.A.R.I-

→ unit = $\text{mol L}^{-1} \text{s}^{-1}$ or $\text{mol L}^{-1} \text{min}^{-1}$ or $\text{mol L}^{-1} \text{h}^{-1}$.

- Q) For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 min . Calculate the average rate of reaction using units of time both in minutes and seconds.

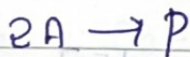
Solⁿ

$\Delta t = 25 \text{ min}$

$$\text{rate} = - \frac{(c_2 - c_1)}{\Delta t} = - \frac{(0.02 - 0.03)}{25} = 4 \times 10^{-4} \text{ M L}^{-1} \text{min}^{-1}$$

or,

$$\text{rate} = \frac{+0.01}{1500} = \frac{1}{1500} \times 10^{-4} \text{ M L}^{-1} \text{s}^{-1} = 6.67 \times 10^{-6} \text{ M s}^{-1}$$

Ex 4.21-

$0.5 \rightarrow 0.4 \text{ mol L}^{-1}$ in 10 min

$$\text{rate} = - \frac{1}{2} \frac{\Delta A}{\Delta t}$$

$$= - \frac{1}{2} \frac{(0.4 - 0.5)}{10}$$

$$= \frac{0.1}{20}$$

$$= \frac{1}{200} \text{ mol L}^{-1} \text{min}^{-1}$$

- Q) Reaction: $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, if the conc. of NO_2 increases by $1.6 \times 10^{-2} \text{ M}$ in 4 s . Calculate:-

(i) Rate of formation/appearance of NO_2 :-

$$\text{R.O.F. of } \text{NO}_2 = + \frac{d[\text{NO}_2]}{dt} = \frac{1.6 \times 10^{-2} \text{ M}}{4}$$

$$= 4 \times 10^{-3} \text{ M s}^{-1}$$

(iv) Rate of Reaction :-

$$\text{rate of R} = - \frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$$

(i) Rate of Appearance of O_2 :-

$$r = \frac{d[O_2]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt}$$

$$= \frac{1}{4} \times 4 \times 10^{-3}$$

$$= 10^{-3} \text{ Ms}^{-1}$$

(ii) Rate of disappearance of N_2O_5 :-

$$\therefore \frac{-1}{2} \frac{d[N_2O_5]}{dt} = \frac{1}{4} \frac{d[NO_2]}{dt}$$

$$\Rightarrow - \frac{d[N_2O_5]}{dt} = 2 \times 10^{-3} \text{ Ms}^{-1}$$

(iii) Rate of R_x^n :-

$$= -\frac{1}{2} \frac{d[N_2O_5]}{dt}$$

$$= 1 \times 10^{-3} \text{ Ms}^{-1}$$

Rate law:-

- The experimental expression of R or R_x in terms of concentration of Reactants is known as Rate law.
- In this expression the rate of a reaction is proportional to the product of molar concentration of reactants with each term raised to the product of molar concentration of reactants with each term raised to the power or exponent that has to be found experimentally.

In a chemical reaction:- $aA + bB \rightarrow \text{Product}$

∴ The rate law is:- Rate $\propto [A]^m \cdot [B]^n$

m and n may or may not be equal to a and b .

$$\text{so, } \boxed{\text{Rate} = k [A]^m \cdot [B]^n}$$

where,

$k \rightarrow$ Rate constant

Rate constant:-

In a chemical reaction,



Acc. to law of Mass action,

$$\text{Rate} = k [A]^{n_1} [B]^{n_2}$$

Acc. to Rate law (experimental concept),

$$\text{Rate} = k [A]^x [B]^y$$

$\left. \begin{array}{l} n, y \rightarrow \text{experimentally} \\ \text{Found} \end{array} \right\}$

IF $[A] = [B] = 1 \text{ mol/L}$,

$$\boxed{\text{Rate} = k}$$

* $\rightarrow$ Rate of Reaction at unit concentration of reactants is called as rate constant or specific reaction rate.

* $\rightarrow$ Rate constant does not depend on concentration of reactants but it depends on temperature and catalyst.

Order of Reaction:-

$\rightarrow$ The sum of powers of concentration of reactants in rate law expression is known as order of reaction.

For the reaction; $aA + bB \rightarrow \text{product}$

Rate law, $R = k [A]^x [B]^y$

$x \rightarrow$ order of rxn w.r.t. $[A]$

$y \rightarrow$ order of rxn w.r.t. $[B]$

$$\boxed{x+y = \text{overall order of rxn}}$$

$\rightarrow$ order of reaction may be zero, positive, negative or fraction

$\rightarrow$ order of Reaction is an experimental quantity.

Unit of rate constant:-

Rate = $k [A]^n$, $n \rightarrow$ overall order of rxn

$$k = \frac{\text{Rate}}{[A]^n} = \frac{\text{mol L}^{-1} \text{s}^{-1}}{(\text{mol L}^{-1})^n} \\ = (\text{mol L}^{-1})^{1-n} \cdot \text{time}^{-1}$$

IF time is in hour,

$$\text{unit of } k = (\text{mol L}^{-1})^{1-n} \text{ h}^{-1}$$

IF time is in minutes,

$$\text{unit of } k = (\text{mol L}^{-1})^{1-n} \text{ min}^{-1}$$

For gaseous reaction unit of k may be = $(\text{atm})^{1-n} \times \text{time}^{-1}$

Zero order	1 st order	2 nd order
unit of $k = \text{mol L}^{-1} \text{time}^{-1}$	unit of $k = \text{time}^{-1}$	unit of $k = (\text{mol L}^{-1})^{-1} \text{time}^{-1}$ $= \text{L mol}^{-1} \text{time}^{-1}$

4.3

For a reaction, $A + B \rightarrow \text{product}$, the rate law is given by,

$r = k [A]^{1/2} [B]^2$, what is the order of the reaction?

Solⁿ

$$R = k [A]^{1/2} [B]^2$$

$$\text{order of rxn} = 1/2 + 2$$

$$= \boxed{2.5}$$

Q) The following data for the reaction $A + B \rightarrow \text{product}$ is given:-

Experiment No.	[A]	[B]	ROD ($\text{mol L}^{-1} \text{s}^{-1}$)
1	1	2	4
2	2	2	4
3	2	4	16

What is the rate law eqⁿ?Solⁿ:-

$$\text{rate} = k [A]^m [B]^n$$

Experiment 1:-

$$4 = k [1]^m [2]^n \quad \text{--- (1)}$$

$$\text{Exp-2:- } 4 = k [2]^m [2]^n \quad \text{--- (2)}$$

$$\text{Exp-3:- } 16 = k [2]^m [4]^n \quad \text{--- (3)}$$

Now divide eqⁿ (1) and (2),

$$\frac{4}{4} = \frac{k [1]^m [2]^n}{k [2]^m [2]^n}$$

$$\Rightarrow 1 = \left(\frac{1}{2}\right)^m$$

$$\Rightarrow 1 = \frac{1}{2^m}$$

$$\Rightarrow \frac{1}{2^0} = \frac{1}{2^m}$$

$$\Rightarrow \boxed{m = 0}$$

Now, divide eqⁿ (2) and (3),

$$\frac{4}{16} = \frac{k [2]^m [2]^n}{k [2]^m [4]^n}$$

$$\Rightarrow \frac{1}{4} = \left(\frac{2}{4}\right)^n$$

$$\Rightarrow \frac{1}{4} = \frac{1}{2^2}$$

$$\Rightarrow \frac{1}{2^2} = \frac{1}{2^n}$$

$$\Rightarrow \boxed{n = 2}$$

So,

$$\text{Rate} = k [A]^0 [B]^2$$

Now, in eqⁿ (1),

$$4 = k [1]^0 [2]^2$$

$$\Rightarrow 4 = k \times 4$$

$$\Rightarrow \boxed{k = 1}$$

So,

$$\text{Rate} = 1 \times 1 \times [B]^2$$

$$= [B]^2$$

Molecularity:-

→ Total number of molecules, atoms or ions (reacting species) participating in an elementary reaction is called as molecularity of Reaction.

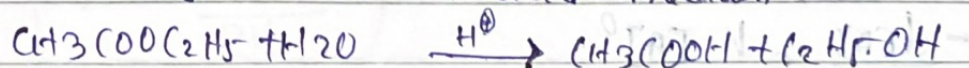
- Molecularity is a theoretical quantity.
- Molecularity can be an integer (1, 2, 3) but it can't be zero or negative or fractional.
- In elementary reaction, molecularity is equal to its order.
- In complex reaction, molecularity of each step of mechanism is defined separately.
- Total molecularity of complex reaction is meaningless.
- In complex reaction, generally molecularity of slowest step is same as order of reaction which can be considered as molecularity of reaction. (except when slowest step contain intermediate).
- Maximum value of molecularity is 3, because ^{changes} of effective collision of more than three molecules is very rare.

Pseudo First order Reaction:-

→ A chemical reaction in which value of order of reaction is one but molecularity is more than one are known as pseudo unimolecular / pseudo first order reaction.

Example:-

Hydrolysis of ester in acidic medium.



$$\text{Rate} = k [\text{CH}_3\text{COO}(\text{C}_2\text{H}_5)] [\text{H}_2\text{O}]$$

Water is in excess ~~from~~ its concentration remains constant during the reaction and $[\text{H}_2\text{O}]$ is taken as constant therefore,

$$\text{Rate} = k' [\text{CH}_3\text{COO}(\text{C}_2\text{H}_5)], \text{ where } k' = k[\text{H}_2\text{O}]$$

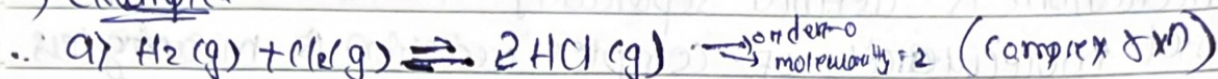
Integrated Rate eqⁿ:-

A) zero order reactions:-

→ Reactions in which rate of reaction remains independent of concentration of the reactant are said to be zero order reactions.

→ zero order reactions are relatively uncommon but they occur ~~on~~ under special conditions. Some enzyme catalysed reactions and reactions which occur on metal surfaces are a few examples of zero order reactions.

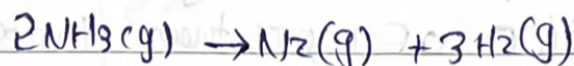
→ Examples



b) Reaction betⁿ acetone and bromine.

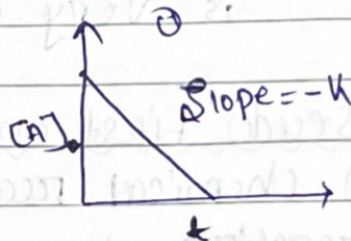
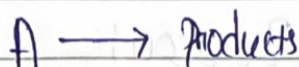
c) Dissociation of HI on gold surface.

d) The decomposition of gaseous ammonia on a hot platinum surface is a zero order reaction at high pressure,



Differential rate eqⁿ

(zero order)



$$\text{rate} = -\frac{d[A]}{dt} \quad \text{--- (1)}$$

According to rate law,

$$\text{rate} = k [A]^0 \quad \text{--- (2)}$$

From eqⁿ (1) and (2),

$$-\frac{d[A]}{dt} = k [A]^0$$

$$\Rightarrow -\frac{d[A]}{dt} = k \times 1$$

$$\Rightarrow -d[A] = k \cdot dt$$

$$\Rightarrow d[A] = -k \cdot dt$$

Integrating both sides,

$$\int_{[A]_0}^{[A]_t} d[A] = -k \int_0^t dt$$

$$\Rightarrow [A]_t - [A]_0 = -kt \rightarrow \text{Integrated rate eqn}$$

$$\Rightarrow [A]_t = [A]_0 - kt$$

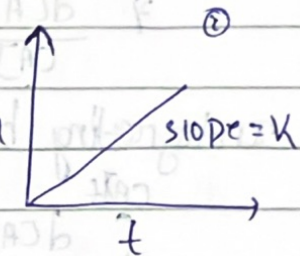
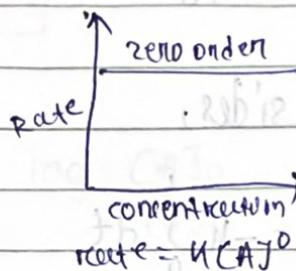
$$\Rightarrow kt = [A]_0 - [A]_t$$

$$\Rightarrow k = \frac{[A]_0 - [A]_t}{t}$$

$$k = \frac{m}{t}$$

$$\Rightarrow [m = kt]$$

$$y = mx + c$$



Half-life: ($t_{1/2}$)

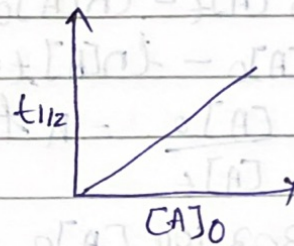
The time taken by the reactant to reduce to half of its initial concentration.

$$At \ t_{1/2},$$

$$[A]_t \rightarrow \frac{[A]_0}{2}$$

$$t_{1/2} = \frac{[A]_0 - \frac{[A]_0}{2}}{k}$$

$$\Rightarrow t_{1/2} = \frac{[A]_0}{2k}$$

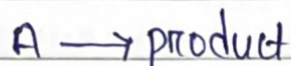


B) First order Reaction:-

Ex¹

- ① $2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$
- ② $\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
- ③ All radioactive decays.

Derivation:-



Differential rate eqⁿ:-

$$-\frac{d[\text{A}]}{dt} = k[\text{A}]^1$$

$$\Rightarrow \frac{d[\text{A}]}{[\text{A}]} = -k dt$$

Integrating both sides,

$$\int_{[\text{A}]_0}^{[\text{A}]_t} \frac{d[\text{A}]}{[\text{A}]} = -k \int_0^t dt$$

$$\Rightarrow \ln [\text{A}]_t - \ln [\text{A}]_0 = -kt$$

$$\Rightarrow \ln [\text{A}]_0 - \ln [\text{A}]_t = kt$$

$$\Rightarrow \ln \frac{[\text{A}]_0}{[\text{A}]_t} = kt$$

$$\Rightarrow 2.303 \log \frac{[\text{A}]_0}{[\text{A}]_t} = kt$$

$$\Rightarrow \boxed{k = \frac{2.303 \log \frac{[\text{A}]_0}{[\text{A}]_t}}{t}} \rightarrow \text{Integrated Rate eq}^n$$

or

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \rightarrow \begin{matrix} a \rightarrow \text{Initial conc.} \\ a-x \rightarrow \text{remaining conc.} \end{matrix}$$

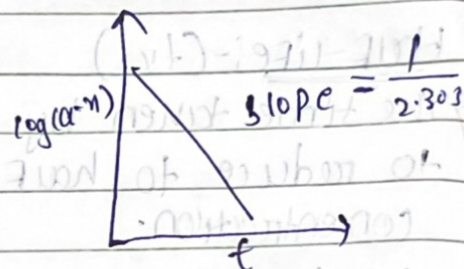
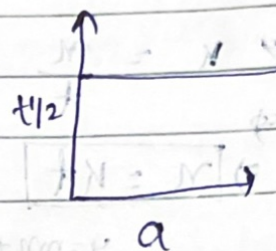
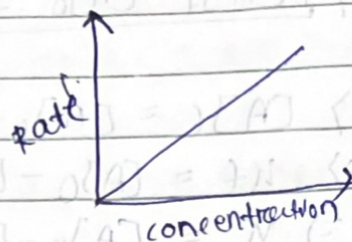
when,

$$t \rightarrow t_{1/2} \text{ if } [\text{A}]_t = \frac{[\text{A}]_0}{2}$$

$$\text{so, } t_{1/2} = \frac{2.303}{k} \log \frac{[\text{A}]_0}{[\text{A}]_0/2}$$

$$\Rightarrow \boxed{t_{1/2} = \frac{0.693}{k}}$$

* First order rxⁿ can never be completed.



$$\text{Ex}^{\text{free}} \quad t_{1/2} \propto \frac{1}{a^{n-1}}$$

$n = \text{overall order}$

Q) 20% of a first order reaction was completed in 5 min. When will 60% of the reaction complete?

solⁿ $t = 5 \text{ min}$

$$\begin{aligned}
 k &= \frac{2.303}{t} \log \frac{[A]_0}{[A]_t} \\
 &= \frac{2.303}{5 \text{ min}} \log \frac{100}{80} \\
 &= \frac{2.303}{5} \log \frac{5}{4}
 \end{aligned}$$

$$k = 0.0446 \text{ min}^{-1}$$

60% completion, $t = ?$

$$\begin{aligned}
 t_{60\%} &= \frac{2.303}{k} \log \frac{[A]_0}{[A]_t} \\
 &= \frac{2.303}{0.0446} \log \frac{100}{40}
 \end{aligned}$$

$$= \frac{2.303}{0.0446} \log \frac{5}{2}$$

$$t_{60\%} = 20.55 \text{ min}$$

Temperature dependence of the Rate of a Reaction:-

→ It has been found that for a chemical reaction with rise in temperature by 10° , the rate constant is nearly doubled.

→ Temperature coefficient (n): It is defined as ratio of rate constant of a reaction at two different temperatures which will be differ by 10°C .

$$n = \frac{k_{T+10}}{k_T} = 2 \text{ to } 3$$

$$\frac{r_2}{r_1} = \frac{k_2}{k_1} = n^{(T_2 - T_1)/10}$$

∴ IF temperature of reaction is not specified then consider 25°C . (IF n is not given consider it as minimum 2)

Arrhenius equation:-

$$k = A e^{-\frac{E_a}{RT}}$$

where,

k = rate constant

A = Arrhenius constant / pre-exponential factor / frequency factor

$E_a \Rightarrow$ Activation energy

$R \rightarrow$ Gas constant

T = Temp. in kelvin

Q) If temperature of a reaction is increased from 10°C to 100°C then how many times rate of reaction will become?

Solⁿ

$$\begin{array}{ccc} 10^\circ\text{C} & \longrightarrow & 100^\circ\text{C} \\ \frac{k_2}{k_1} = \frac{A_2}{A_1} = M^{\Delta T/10} & & \Delta T = 100^\circ\text{C} - 10^\circ\text{C} \\ & & = 90^\circ\text{C} \end{array}$$

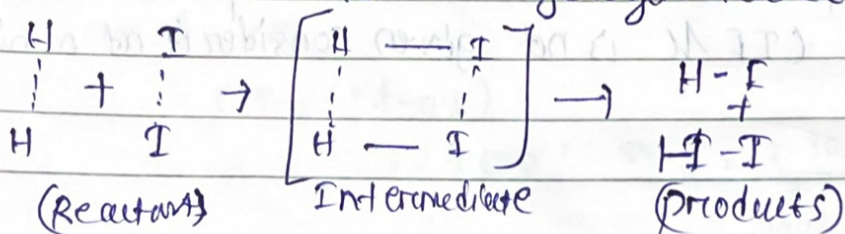
$$\Rightarrow \frac{k_2}{k_1} = 2^{90/10}$$

$$\Rightarrow \boxed{k_2 = 2^9 \text{ times of } k_1}$$

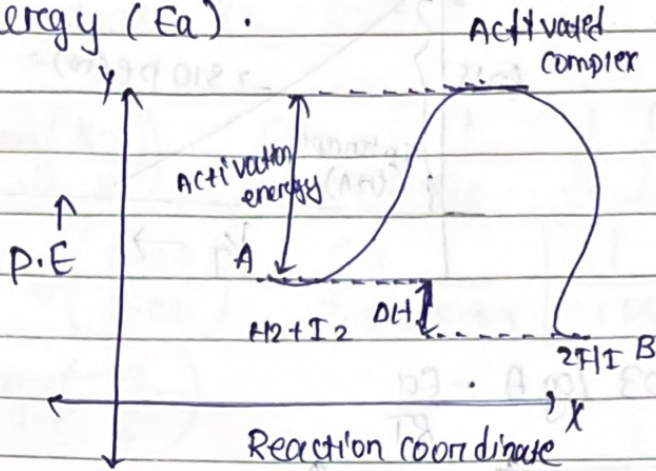


$\rightarrow$ According to Arrhenius, this reaction can take place only when a molecule of hydrogen and a molecule of iodine collide to form an unstable intermediate.

$\rightarrow$ It exists for a very short time and then breaks up to form two molecules of hydrogen iodide.

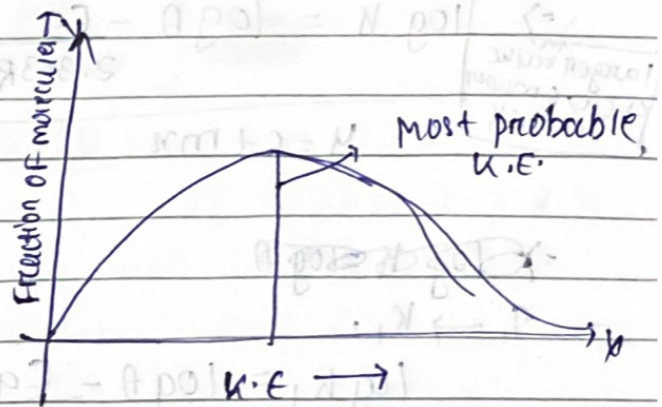


→ The energy required to form this intermediate, called activated complex (C), is known as activation energy (E_a).



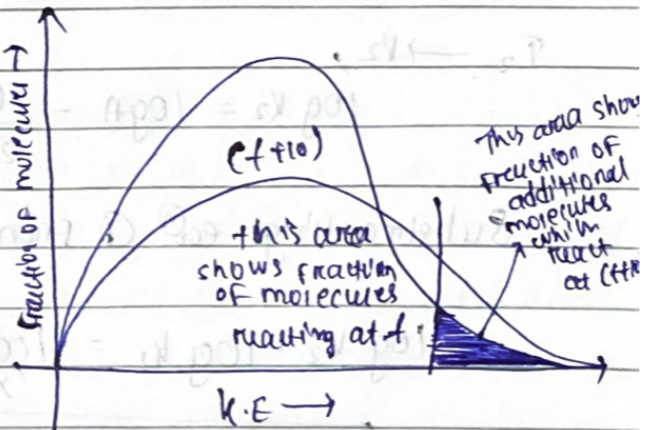
Maxwell-Boltzmann distribution:-

→ The peak of the curve corresponds to the most probable kinetic energy, i.e. kinetic energy of maximum fraction of molecules.



→ Increasing the temperature of the substance increases the fraction of molecules, which could with energies greater than E_a .

→ It is clear from the diagram that in the curve at $(t + t_0)$, the area showing the fraction of molecules having energy equal to or greater than E_a gets doubled according to doubling the rate of a Reaction.



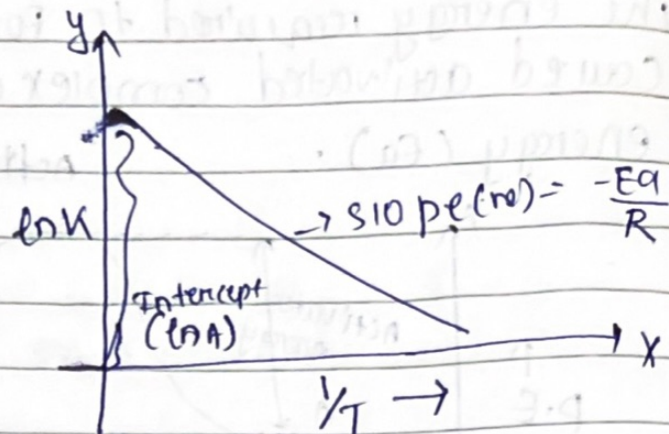
Arrhenius Equation:-

$$k = A e^{-\frac{E_a}{RT}}$$

taking $\ln$ both sides,

$$\ln k = \ln A - \frac{E_a}{RT}$$

comparing with $y = c + mx$

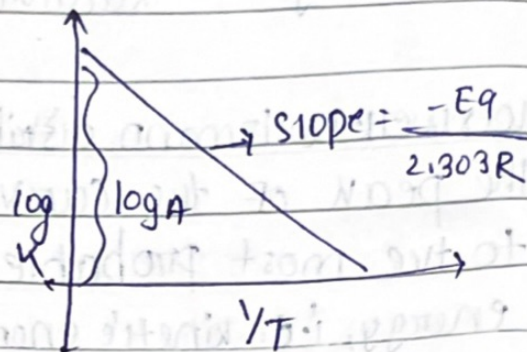


$$\rightarrow 2.303 \log k = 2.303 \log A - \frac{E_a}{RT}$$

$\Rightarrow$ $\log k = \log A - \frac{E_a}{2.303RT}$

larger value of E_a means smaller k

$y = c + mx$



~~$\log k = \log A$~~

$T_1 \rightarrow k_1$

$$\log k_1 = \log A - \frac{E_a}{2.303RT_1} \quad \text{--- (i)}$$

$T_2 \rightarrow k_2$

$$\log k_2 = \log A - \frac{E_a}{2.303RT_2} \quad \text{--- (ii)}$$

Subtracting eqⁿ (i) from (ii),

$$\log k_2 - \log k_1 = \log A - \frac{E_a}{2.303RT_2} - \log A + \frac{E_a}{2.303RT_1}$$

$$\Rightarrow \log \left(\frac{k_2}{k_1} \right) = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Factors Affecting ROR:-

1) Nature of reactant:-

(a) Physical state of reactant:-

→ Increasing order of Rate of reaction [solid < liquid < gas]
(Intermolecular attractive force decreases which provides more freedom for collisions).

(b) Physical size of particles (if reactant is solid):-

↑ Rate of Reaction $\propto$ physical size $\propto$ surface area ↑

(c) Chemical nature of reactant:-

- For different reacting species number of bonds broken and their bond energies are different. Therefore requirement of activation energy is also different.
- Low Reactions having less value of activation energy will take place at faster rate.

2) Concentration of Reactant:-

→ Rate of Reaction $\propto$ concentration of reactant.

3) Pressure:-

→ Effect of pressure on ROR is negligible when reactants are solid ~~and~~ on liquid. But if reactants are in gaseous state then ROR increases on increasing pressure because number of effective collisions increases.

4) Temperature:-

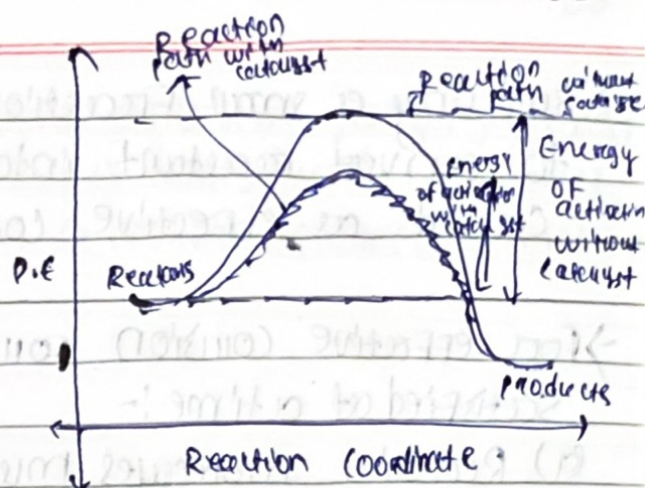
→ on increasing temperature, rate of reaction ↑ whether the reaction is exothermic or endothermic. when temperature ↑, K.E of molecules ↑, number of activated molecules ↑, thus rate of Reaction increases.

5) Presence of catalyst:-

→ In presence of catalyst, E_a of Reaction decreases and rate of reaction increases.

+ve catalyst $\rightarrow E_a \downarrow$, ROR $\uparrow$

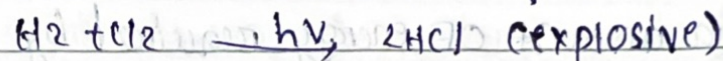
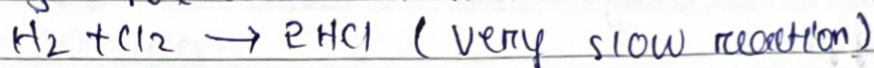
-ve catalyst $\rightarrow E_a \uparrow$, ROR $\downarrow$



6) Exposure to radiation:-

→ Rate of some reactions also increases when reaction are carried out in the presence of radiation. only for photochemical Reaction

e.g. Formation of HCl

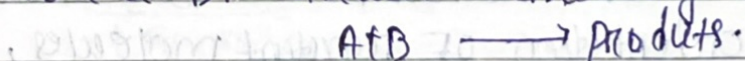


Collision theory of chemical reactions:-

→ This theory was given by Max Trautz and William Lewis.

→ According to it, for a reaction to occur there must be collisions in betⁿ reacting molecules. Total number of collisions per second in unit volume is called collision frequency (Z). Generally its value is very high for gaseous reaction (10^{25} to 10^{28} collisions/sec cm^3).

For a bimolecular elementary reaction,



$$\text{Rate} = P Z_{AB} e^{-E_a/RT}$$

where,

Z_{AB} = collision frequency of reactants A and B

$e^{-E_a/RT}$ = fraction of molecules with energies $\geq E_a$

→ But only a small fraction of these collisions are capable to convert reactant into product. These collisions are called as effective collisions.

→ For effective collision following two conditions must be satisfied at a time :-

- a) Reacting molecules must possess a minimum amount of energy.
- b) Proper orientation of collision.

Threshold energy:-

→ The minimum energy which must be possessed by reacting molecules for a chemical reaction to occur.

Activation energy:-

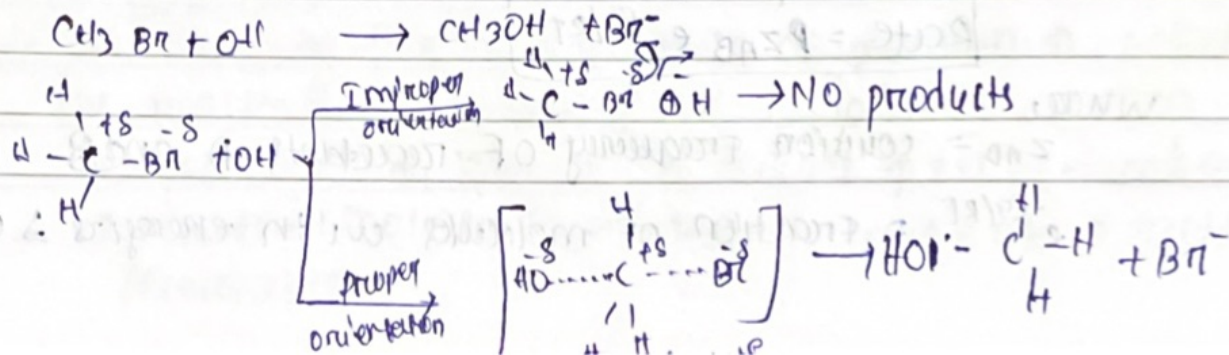
→ The minimum extra amount of energy required by reactant molecules for converting into products.

- Activation Energy depends upon:-

- 1) Nature of Reagent.

-1 For different reactants, number of bonds and bond energies are different, therefore E_a will also be different. Reactions which have less E_a , take place at faster rate.

For example, Formation of methanol from bromomethane depends upon the orientation of reactant molecules,



→ To account for effective collisions, another factor p called the probability or steric factor is introduced. It takes into account the fact that in a collision molecules must be properly oriented i.e.,

$$\text{Rate} = PZ_{AB}e^{-E_a/RT}$$

→ Thus, in collision theory E_a and proper orientation of the molecules together determine the criteria for an effective collision and hence the rate of a chemical reaction.

Limitations of collision theory:-

- (i) This theory is mainly applicable for gaseous reactions and also for solutions in which reacting species are molecules.
- (ii) This theory is mainly applicable for simple bi molecular reactions but fails for complex reactions.
- (iii) It considers molecules to be hard spheres and ignore structural aspect of molecules.